

DGEBA-Grafted Polyaniline: Synthesis, Characterization and Thermal Properties

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ABSTRACT: The utilization of conducting emeraldine salt (PANI-ES) and intrinsic leucoemeraldine polyaniline (PANI-LEB) in the synthesis of DGEBA-grafted PANI via anionic copolymerization is described. The structures of copolymers obtained were characterized by FTIR, ¹³C and ¹H NMR. The extent of grafting was verified by THF Soxhlet (solvent extraction). The thermal properties of these new copolymers were described and their con-

ductivities were reported. Results obtained indicated that the graft copolymer exhibited higher electrical and thermal conductivities than that of the blend counterpart. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 49–58, 2011

Key words: graft copolymers; polyaniline; DGEBA; FT-IR; NMR

INTRODUCTION

Epoxy resins are well known for some unique properties, including high degree of chemical and solvent resistance, outstanding adhesion to a broad range of surfaces, impact resistant, low order of shrinkage on cure, and high mechanical strength. They have been used as adhesives, coatings, reinforced plastics, and resin matrices for advanced composites.¹ However, epoxy resins are too brittle to be utilized alone and thus other materials have to be added in to enhance or compensate its weaknesses.

Various materials have been used to improve the mechanical and thermal properties of epoxy resins such as oligomers and polymer modifiers,² organosiloxane polymers,^{3–5} organophosphorus compounds,^{6,7} etc. Most of these materials were generally utilized to improve toughness, reduce thermal stress, flexural modulus, and coefficient of thermal expansion (CTE) of epoxy final products.

In electronic application, conductive epoxies were required as encapsulation materials for electronic devices because of their superior mechanical, thermal, and electrical properties. However, the issues of dissipation of high thermal load, corrosion, low elec-

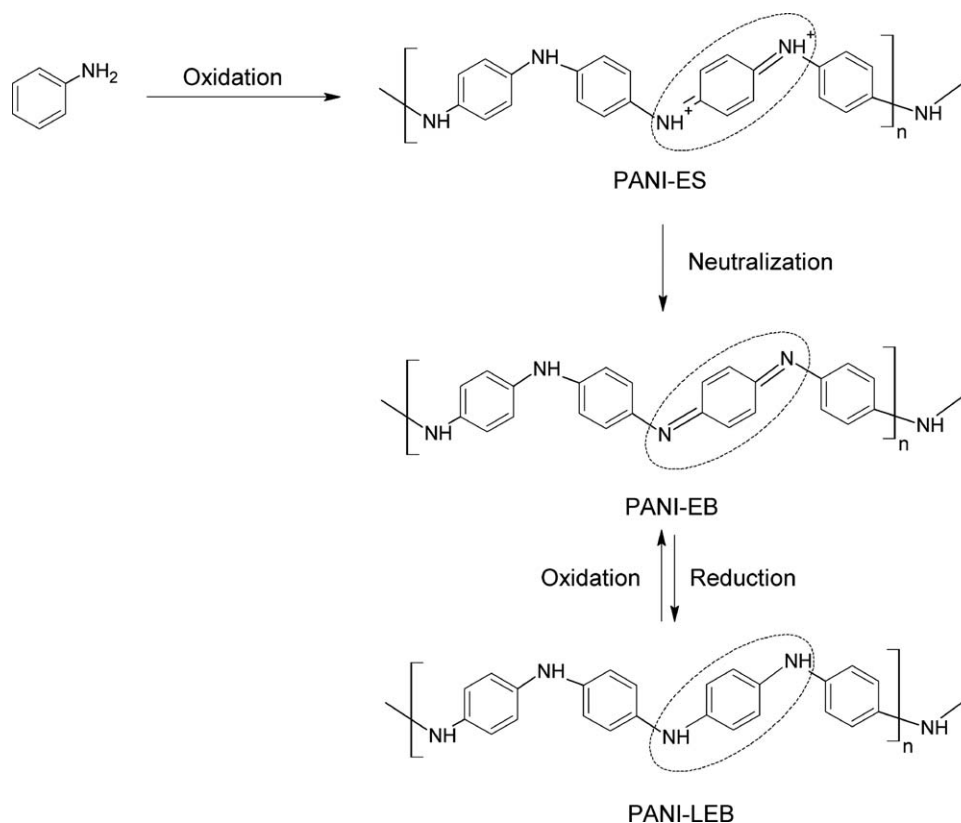
trical and thermal conductivity, etc., in electronic packaging still exist. As a result, materials for high reliability of encapsulation, high thermal conductivity, and low dielectric constant are required.⁸ Inorganic fillers are usually incorporated into the epoxy molding compounds (EMC) as a conductor to enhance the conductivity of the compounds.

The synergic effects such as matrix-fillers compatibility, dispersion of fillers in epoxy matrix, and size of fillers, which is in micron dimension etc. have limited the performance of EMC. Thus, alternative routes were explored to replace some of the materials such as inorganic fillers to organic fillers and the findings were quite promising. For examples, organic fillers such as polyaniline (PANI) can be utilized as conductive adhesive materials,⁹ electrical conductive resin,^{10,11} and electromagnetic interference (EMI) shielding materials.¹² Recently, Lu et al.¹³ found that PANI/epoxy resin composite had high value of dielectric constant and thus was applied as an embedded capacitor material.

For most method employed, PANI was usually blended together with epoxy resin to form composite as their final product because it is believed that properties of both polymers are complement with each other while maintaining its own unique properties. In this research, we utilized grafting copolymerization technique to produce the diglycidyl ether bisphenol A (DGEBA) grafted PANI copolymer. The graft copolymerization was carried out through ring opening polymerization of epoxide via *N*-alkylation which was based on previous studies.^{14–17} The

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Scheme 1 Polymerization of aniline monomer to emeraldine salt polyaniline (PANI-ES) followed by emeraldine base polyaniline (PANI-EB) and leucoemeraldine base polyaniline (PANI-LEB).

composites that are produced via graft copolymerization are expected to have better mechanical, thermal, and electrical properties compared with that of its polymer blend counterpart. This can be attributed to the grafting between both host polymers thus increases the synergistic effects of the resultant composites.

Grafting of DGEBA onto PANI in different oxidation states particularly in emeraldine salt polyaniline (PANI-ES) and leucoemeraldine base polyaniline (PANI-LEB) have been studied. Molecular structures of PANI-LEB-g-DGEBA and PANI-ES-g-DGEBA copolymers were characterized by FTIR and NMR spectroscopies while the extent of graft copolymerization was verified by using THF Soxhlet extraction. The thermal properties of the copolymers were determined by DSC and thermal conductivity tester. The four point probe method was used to measure the electrical conductivity of copolymers.

EXPERIMENTAL

Materials

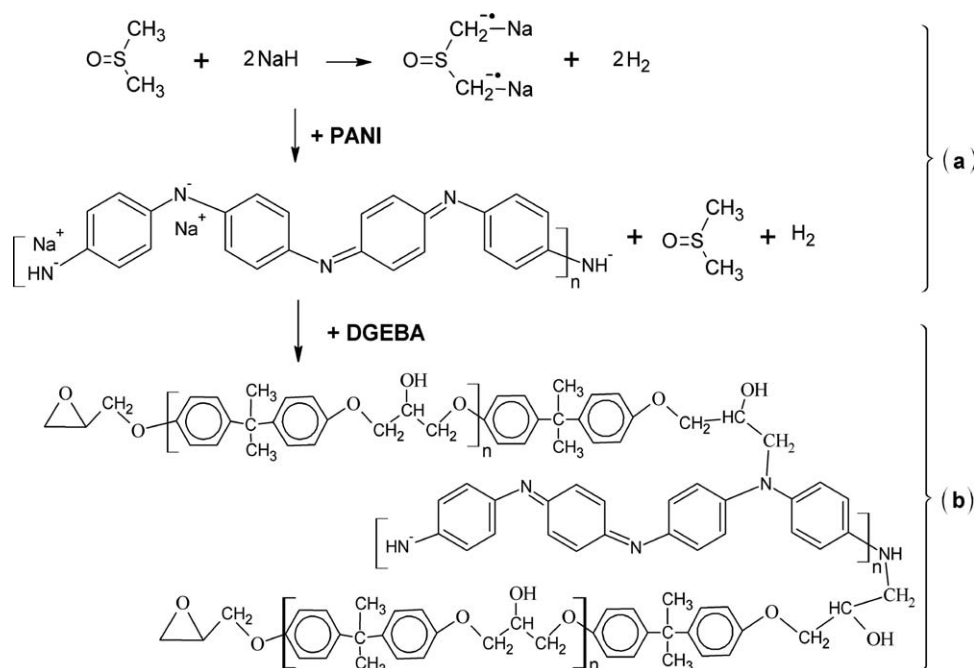
Diglycidyl ether bisphenol A (DGEBA) with trade name EPIKOTE™ Resin 828 was supplied by the ASA Chem. This product is a medium viscosity liquid epoxy resin with epoxy values of about 0.53 mol/100 g and epoxy equivalent of 187 g/equivalent. The cur-

ing agent used was a polyetheramine type hardener (EPIKURE F205) which was also supplied by ASA Chem. Aniline, ammonium peroxydisulphate (APS) and hydrazine monohydrate were analytical grade supplied by Alfa Aesar. Hydrochloric acid (HCl), ammonium hydroxide (NH₄OH), and methanol were provided by Tedia Company, Inc. Sodium hydride (NaH) was supplied by BDH Chemical and DMSO was made in Lab Scan Analytical Science. Aniline was distilled at 182°C until colorless prior to use. All other reagents were used as received.

Synthesis

Polyaniline preparation

The preparation of emeraldine salt polyaniline (PANI-ES) was adapted from the report by Zeng and Ko¹⁸ with APS as the oxidant. Aniline (10 mL) and APS (24.5 g) were prepared separately in 1.0M HCl (150 mL) where the aniline:APS molar ratio was fixed at 1 : 1. The aniline hydrochloride was pre-cooled in an ice bath for 30 min and this was followed by addition of APS solution. After 3.5 h of reaction, the greenish black precipitates were filtered, rinsed with excess water and methanol. This was followed by drying in an oven at 80°C for 24 h. PANI-ES was later neutralized with excess amount



Scheme 2 Schematic representation of graft copolymerization of PANI and DGEBA (a) PANI underwent metalation reaction (b) Formation of grafting on the center and chain end of PANI molecular structure.

of 1.0M NH_4OH and washed with excess water followed by methanol to obtain the emeraldine base polyaniline (PANI-EB). Methanol was used to remove the oligomers which formed during PANI-ES synthesis. The reduced form of polyaniline, leucoemeraldine base (PANI-LEB) was prepared by using hydrazine monohydrate. The reaction was carried out under nitrogen atmosphere for 5 h. The light blue precipitates were washed thoroughly with distilled water and methanol followed by drying in an oven for 1 h at 80°C . The polymerization of aniline monomer to PANI-LEB was represented in Scheme 1.

Graft copolymerization

The graft copolymerization was modified from the reports by Yamaguchi et al.^{16,17} NaH (190 mg, 7.95 mmol) was dissolved in DMSO (40 mL) in a three neck reactor to prepare the sodium methylsulfinyl carbanion solution. The reaction flask was kept under nitrogen atmosphere throughout the subsequent reactions by a constant flow of nitrogen gas. The mixture was stirred at 75°C for 24 h until all the NaH was completely dissolved. This was followed by addition of PANI-LEB (650 mg, 6.99 mmol) into the reaction with stirring for 24 h at 40°C . The dark blue solution was cooled to 30°C before DGEBA (6.50 g 33.4 mmol) was added into it. The reaction was continued for another 24 h. The distilled water was poured into the reaction flask, under vigorous stirring to precipitate the copolymers. The black pre-

cipitates were recovered on a filter paper by using vacuum pump and washed excessively with distilled water and methanol to remove the DMSO solvent and unreacted DGEBA monomer. The black precipitates were later dried in an oven at 80°C for 48 h. The product obtained was labeled as PANI-LEB-g-DGEBA copolymer. The same procedure was employed to prepare the PANI-ES-g-DGEBA copolymer by replacing the PANI-LEB with PANI-ES (1.00 g, 10.75 mmol) where the molar ratio of DGEBA: PANI was fixed to 5 : 1 for both copolymers. The schematic representation of graft copolymerization of PANI and DGEBA is described in Scheme 2.

Preparation of cured graft copolymer

Both DGEBA and copolymers were cured with hardener in a metal mold in an oven at 80°C for 2 h followed by post curing at 120°C for 2 h prior for thermal and electrical conductivity measurement. A sample of polymer blend which contained 5 wt % PANI-ES as filler in DGEBA matrix was also prepared in the same way for comparison purpose.

Characterization

The FTIR spectra were recorded on a GX Perkin-Elmer Infrared Spectrometer using KBr discs in the range of 4000 cm^{-1} to 370 cm^{-1} . The ^1H and ^{13}C NMR spectra were obtained through the ECP 400 model Jeol FT-NMR 400 spectrometer using deuterated chloroform (CDCl_3) as solvent. In the case of

gel content estimation, ~ 0.3 g of each sample was weighed exactly and placed in a thimble which later underwent Soxhlet extraction for 24 h using THF as solvent. After the extraction, the thimble was dried in an oven at 90°C until constant weight was achieved. The gel content is calculated using the Eq. (1):

$$\text{Gel content(\%)} = \frac{\text{Weight after extraction}}{\text{Initial weight}} \times 100 \quad (1)$$

The thermal behavior of the DGEBA and copolymers were studied by differential scanning calorimeter (Mettler Toledo DSC 822e) using the heating rate of $10^\circ\text{C}/\text{min}$ in temperature range of -50°C to 600°C . The four point probe method which utilized Jandel Universal Probe, Keithley 175A multimeter and Keithley 220 Programmable Current Source were used to measure the electrical conductivity. The bulk density was determined by using the Mirage Electronic Densitometer (MD 200S). Thermal conductivity measurement was conducted on Netzsch LFA 447 using InSb as sensor with graphite coating on both surfaces of palletized sample and pyroceram 9606 as standard sample for heat capacity change, C_p determination. Thermal conductivity (k) at 303 K was calculated from the thermal diffusivity (α), specific heat capacity (C_p), and densities (ρ) of the palletized sample using the Eq. (2):

$$k = \rho\alpha C_p \quad (2)$$

RESULTS AND DISCUSSION

Graft copolymerization of PANI with DGEBA

Polyaniline of two different oxidation states, which were emeraldine salt (ES) and leucoemeraldine (LEB) were used to study the grafting reaction with DGEBA. The sodium methylsulfinyl carbanion solution which was prepared by dissolving NaH in DMSO was used to cause metalation reaction on PANI. The reaction was illustrated in Scheme 2(a). This mechanism was reported by Evers et al.¹³ and Yamaguchi et al.^{16,17} Yamaguchi et al.¹⁶ described that deprotonation of NH groups of the PANI chains took place after the addition of PANI into the sodium methylsulfinyl carbanion solution, and thus created more N^- anions on PANI backbone chains. These anions later promoted β -scission on the epoxide rings of DGEBA, followed by ring opening polymerization as shown in Scheme 2(b). Both PANI-LEB-g-DGEBA and PANI-ES-g-DGEBA copolymers can be obtained in this way.

In this work, we found that samples of PANI with different oxidation states used to prepare copolymers with DGEBA showed different level of cross-

link besides desired grafted sections and unavoidable side reaction, DGEBA homopolymerization. The homopolymerization is expected to occur simultaneously during grafting copolymerization of PANI with DGEBA, due to the presence of reactive hydroxyl group on the DGEBA. This showed that anionic grafting technique used in this work was unable to prevent side reaction such as crosslinking and homopolymerization from occurring as also reported by Noshay and McGrath.¹⁹

In addition, separation of homopolymerization products was difficult to be carried out. This could be because homopolymerization can happen on the same PANI chains which had grafted DGEBA at the other end. The resultant ether linkages due to homopolymerization are not easily removed by methanol and water. PANI-g-DGEBA copolymer of partially cured condition makes the homopolymer even more difficult to be separated out from the copolymer.

Besides, PANI-LEB-g-DGEBA was found solidified in the reactor before the reaction was quenched, while PANI-ES-g-DGEBA was still in gel form after 24 h of copolymerization. It is believed that the PANI-LEB which was utilized to form copolymer with DGEBA has been oxidized to typical PANI-EB. During the metalation reaction, the nucleophilicity of the nitrogen was increased by conversion to the anion and thus these unstable emeraldine anions will form more crosslinked sections via intermolecular Michael reaction where N^- added to the $\text{C}=\text{C}$ of another quinoid rings.²⁰ PANI-ES-g-DGEBA copolymer was also expected to have few partially cross-linked sections.

FTIR spectroscopy

The FTIR spectra of PANI-LEB-g-DGEBA copolymer exhibited most of the characteristic peaks of PANI-LEB and DGEBA. There was also indication of new functional groups due to grafting and crosslink formation. PANI-ES-g-DGEBA copolymer which was synthesized by incorporating PANI-ES with DGEBA was found to display similar characteristic peaks to those of PANI-LEB-g-DGEBA copolymer, which was reported elsewhere.²¹

The presence of PANI in both PANI-LEB-g-DGEBA and PANI-ES-g-DGEBA copolymers was identified and it differed by about 1 to 5 cm^{-1} for the same characteristic IR peak. The absorption peaks at 1606 and 1508 cm^{-1} in PANI-LEB-g-DGEBA spectrum were due to $\text{C}=\text{C}$ stretching of quinoid rings and benzenoid rings respectively. The $\text{C}-\text{N}$ stretching mode was represented by peak at 1292 cm^{-1} while peak 1182 cm^{-1} was attributed to the $\text{C}-\text{H}$ bending of aromatic rings. Peak at 828 cm^{-1} was due to the $\text{C}-\text{H}$ out of plane bending of *p*-disubstituted benzene rings.^{18,22}

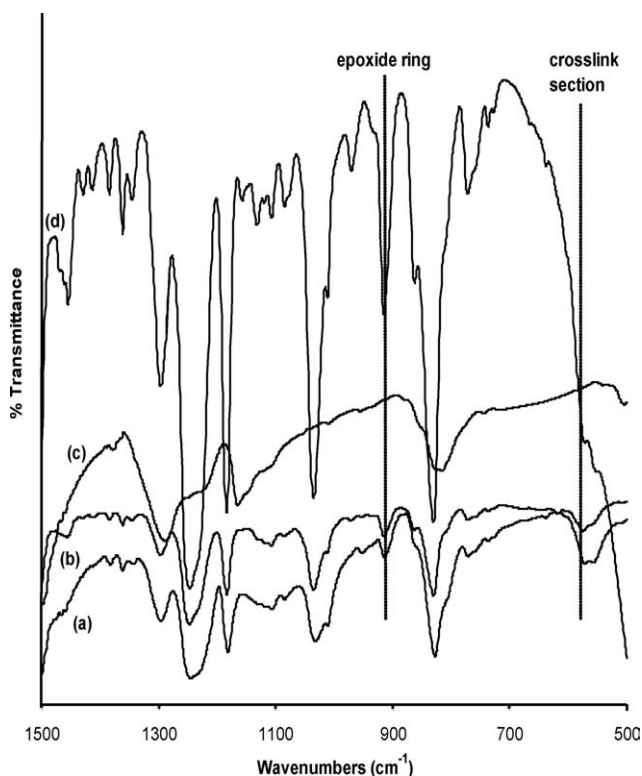


Figure 1 FTIR spectra of (a) PANI-LEB-g-DGEBA copolymer (b) PANI-ES-g-DGEBA copolymer (c) PANI-LEB (d) DGEBA.

The DGEBA which formed graft copolymer with PANI consists of bisphenol A and diglycidyl ether moieties. The absorption peaks at 3492, 1298, and 737 cm^{-1} are attributed to the OH stretching, OH deformation and OH out of plane deformation vibration of the secondary alcohol functional group in DGEBA, respectively. The CO stretching mode displays multiple peaks that are present at 1132, 1108, and 1085 cm^{-1} , due to the coupling with the nearby carbon.²²

The gem-dimethyl functional group, $\text{C}(\text{CH}_3)_2$ in bisphenol A moiety exhibited two peaks at 2967 and 2872 cm^{-1} which are assigned to the CH_3 asymmetrical and symmetrical stretching vibration, respectively. The methylene ether, OCH_2 , which linked the bisphenol A moiety with epoxide ring, displayed two absorption peaks at 2928 and 2872 cm^{-1} due to the asymmetrical and symmetrical CH_2 stretching, respectively. The deformation vibration modes of methyl group can be observed in the region of 1460–1345 cm^{-1} .

The peaks at 1607, 1582, 1511, and 1456 cm^{-1} are assigned to the skeletal vibration modes of aromatic ring. The CH stretching vibration of aromatic rings is detected at 3056 cm^{-1} . Meanwhile, the presence of *para*-disubstituted benzene is confirmed by the appearance of peak at 831 cm^{-1} . Methyl aromatic ether was found to have two strong bands due to

asymmetric and symmetric COC stretching vibration peaks 1247 and 1036 cm^{-1} , respectively. The peaks at 915 cm^{-1} and 772 cm^{-1} are attributed to the epoxide ring vibration. The FTIR spectra of the resultant copolymers were dominantly influenced by the constitution of DGEBA.

For the identification of grafting, it can be seen that the peak due to the C–N stretching of the secondary aromatic group of PANI-LEB appeared at 1376 cm^{-1} [Fig. 1(c)]. The grafting between PANI with DGEBA was expected to exhibit a new peak in the region of 1380–1265 cm^{-1} attributable to C–N stretching of tertiary aromatic amine group. It was reported that the reaction between secondary amine with epoxide will produce a tertiary aromatic amine group.^{23,24} This new functional group was expected to emerge as a result of the formation of grafted section between PANI and DGEBA. Unfortunately, the peak of this functional group was overlapped by the peaks of other functional groups such as O–H, $\text{C}(\text{CH}_3)_2$, and OCH_2 from bisphenol A and diglycidyl ether moiety [Fig. 1(a,b)]. By the way, the peaks due to crosslinking still can be seen in the FTIR spectra of copolymers.

Figure 1(a,b) which represented the spectra of the copolymers exhibited a new peak at about 574 cm^{-1} which was not found in the IR spectra of either DGEBA or PANI. This peak was believed to be due to the 1,2,4-trisubstituted benzene groups and it was assigned as crosslinked section as a result of the intermolecular Michael reactions on quinoid rings of PANI.²⁰

NMR spectroscopy

In this work, ^{13}C and ^1H NMR spectroscopy was used to characterize the molecular structure of PANI-ES-g-DGEBA and PANI-LEB-g-DGEBA copolymers. Both copolymer exhibited similar ^{13}C and ^1H spectra. As shown in Figure 2, the resonance peak of residual carbon of deuterated chloroform appeared in the range of δ_c 77.5–76.9 ppm.^{25,26}

The assignments of ^{13}C NMR spectrum of PANI-LEB-g-DGEBA copolymer was based on the works reported by other researches.^{14,17,25–29} The carbons of glycidyl terminal groups were represented by resonance peaks at δ_c 44.9 (C_1), 50.4 (C_2), and 68.9 ppm (C_3). The aromatic carbons in copolymer have resonance peaks at δ_c 156.5 (C_4), 143.8 (C_7), 127.9 ($\text{C}_6, \text{C}_{11}$), and 114.1 ppm ($\text{C}_5, \text{C}_{10}$). Aromatic carbons with high intensity at δ_c 127.9 and 114.1 ppm showed that these carbons were bonded to hydrogen atom. Meanwhile, aromatic carbons which bonded to another atom that has higher electronegativity than hydrogen atom displayed low intensity peaks as it centered at δ_c 156.5 and 143.8 ppm. The resonance peak at δ_c 31.2 ppm (C_9) and δ_c 41.9 ppm (C_8)

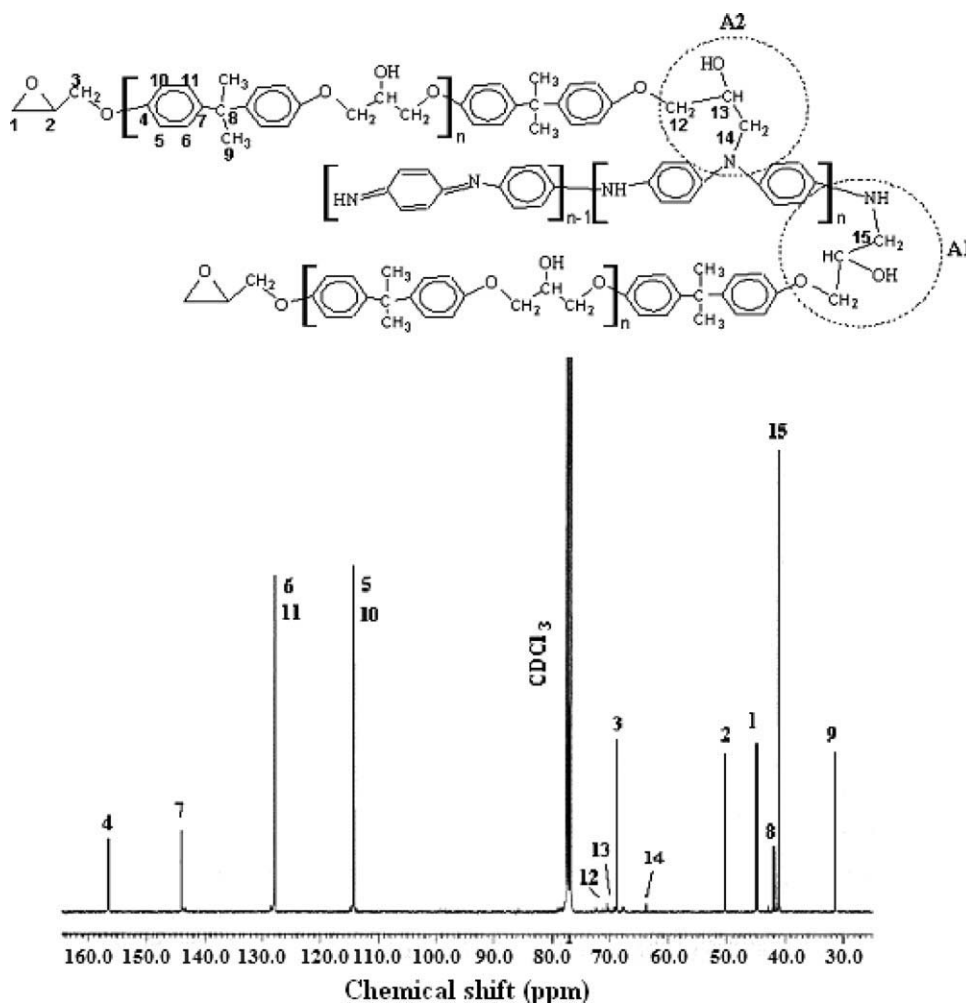


Figure 2 Assignments of ^{13}C NMR chemical shift for PANI-LEB-g-DGEBA copolymer with A1 and A2 represented the grafting on the chain end and center of PANI backbones, respectively.

referred to the methyl carbons and quaternary carbon of bisphenol A moiety respectively.

The grafting was expected to occur on the center and chain end of PANI structure. The grafting on the center of PANI structure was represented by A2 which have resonance peaks at δ_c 63.9 (C₁₄), 69.3 (C₁₃) and 70.5 ppm (C₁₂). Meanwhile the grafting on the chain end of PANI structure can be determined by the chemical shift at δ_c 41.1 ppm (C₁₅) which was represented by A1. The assignment of ^{13}C chemical shift on copolymer molecular structure was illustrated in Figure 2. For the crosslinked section, the carbon resonance peaks for 1,2,4-trisubstituted benzene could not be identified as the percentage of crosslinked formation were expected to be much lesser. In addition, the resonance peaks were possibly overlapped by peaks of the *para*-disubstituted benzene from bisphenol A moiety and benzenoid rings of PANI in the range of δ_c 100–150 ppm.

For PANI-ES-g-DGEBA copolymer, the ^{13}C chemical shift was similar to that of PANI-LEB-g-DGEBA copolymer. The determination of ^{13}C chemical shift

of PANI-ES-g-DGEBA was as follows (δ_c in ppm from TMS = 0): carbon aromatic (156.5, 143.8, 127.9, 114.1 ppm), carbon of epoxide ring (68.9, 50.4, 45.0 ppm), and carbon of gem-dimethyl (41.9, 31.2 ppm). The ^{13}C chemical shift of grafting bonds also did not change and remained constant at δ_c 41.1 ppm as well as 70.5, 69.3, and 63.9 ppm. This explains that the PANI-ES-g-DGEBA copolymer also underwent grafting reaction.

Besides grafting, the indication of side reaction such as DGEBA homopolymerization also can be found in the ^{13}C NMR spectrum of PANI-ES-g-DGEBA but not in that of the PANI-LEB-g-DGEBA copolymer. Mijovic et al. explained that DGEBA homopolymerization occurred under the presence of Lewis base catalyst or acidic medium, high temperature as well as excess of epoxide groups.³⁰ Lack of active N-H formed in PANI-ES as compared in the PANI-LEB, and the presence of Cl⁻ anions in PANI-ES contributed to the formation of ether linkages which later known as DGEBA homopolymerization. The ether linkages were formed as a product from

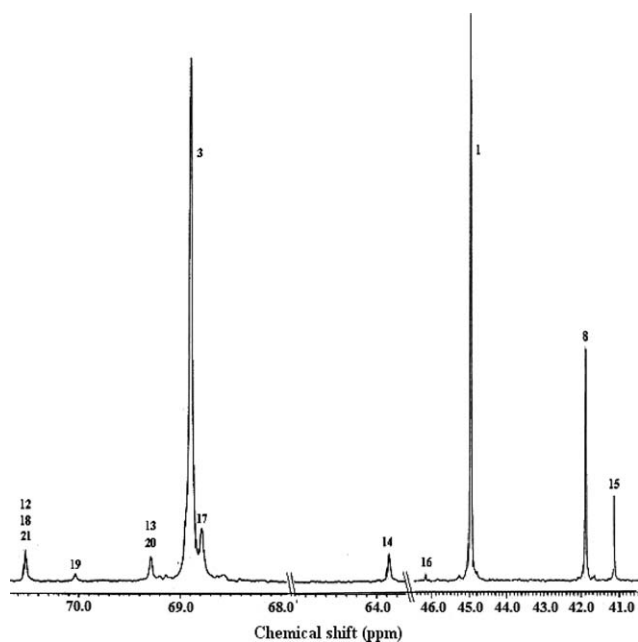


Figure 3 ^{13}C NMR spectrum of PANI-ES-g-DGEBA copolymer where DGEBA homopolymer signals were found.

the reaction between terminal β -hydroxyl of the resultant grafting with the excesses DGEBA.

The resonance peaks of DGEBA homopolymer formed in PANI-ES-g-DGEBA copolymer were in the range of δ_c 75.0–68.0 ppm (Fig. 3). The assignments of ^{13}C chemical shift for DGEBA homopolymer were as follows: δ_c 46.2 (C_{16}), 68.8 (C_{17}), 70.0 (C_{19}), 70.5 (C_{18} , C_{21}), and 69.3 ppm (C_{20}). The formation of ether linkages was assigned as E in Figure 4 and its formation was expected to cause chemical shift of nearby aromatic carbons shifted ± 0.1 ppm. The aromatic carbons next to ether linkages possibly have resonance peaks at δ_c 156.4 (C_{22}), 143.9 (C_{25}), 127.9 (C_{23}), and 114.0 ppm (C_{24}).

The ^1H NMR spectra supported the assignment of ^{13}C chemical shift of both copolymers where resonance peaks of the DGEBA homopolymer were not found in PANI-LEB-g-DGEBA copolymer. The chemical shifts for ^1H NMR spectrum of diglycidyl ether group and aromatic ring of copolymers appeared in between δ_H 2.7–4.2 ppm and δ_H 6.8–7.2 ppm, respectively. The signal at δ_H 1.6 ppm was attributed to the proton of methyl groups in bisphenol A moiety. All these resonance peaks indicated the existence of DGEBA in copolymers. During the copolymerization, it was expected that some oligomers were formed. The aliphatic protons of oligomers were found to have resonance peak at δ_H 4.0 ppm as reported elsewhere.³¹

^1H NMR analysis also indicated that two types of grafting occurred in the copolymers. The A2 grafting which formed at the center of PANI molecular structure was produced via secondary aromatic amine-

epoxide ring reaction. It later created the tertiary aromatic amine group where the chemical shift can be seen at δ_H 2.99 ppm. The A1 grafting which resulted from primary aromatic amine-epoxide ring reaction has resonance signal at about δ_H 2.6 ppm together with the proton of β -hydroxyl terminal in the range of δ_H 1.7–1.9 ppm. It was found that the methylene protons which grafted on N atoms appeared in between δ_H 2.6 and 3.0 ppm where sharp singlet pattern can be seen. The pattern was due to the electrical quadrupole moment of the nitrogen nucleus.²⁵

The protons of ether linkages due to DGEBA homopolymerization have resonance signal in the range of δ_H 2.7–4.4 ppm. The ^1H chemical shift of $\text{CH}_2\text{-N}$ (H_o) in E formation was found to have higher value than the proton of $\text{CH}_2\text{-N}$ (H_k) in A1 grafting. The formation of ether linkages was expected to cause the H_o shifted to lower field as the electron density on grafted area was decreased thus deshielding the H_o .

For crosslinked section, the ^1H chemical shifts were found to be overlapped by the resonance signals of *para*-disubstituted benzene group in the range of δ_H 6.5–8.0 ppm. This can be explained by the fact that the ^1H in crosslinked section was found located in the same chemical environment and under the same influence of magnetic field as *para*-disubstituted benzene.

Gel content

From the molecular structure characterization, both PANI-ES-g-DGEBA and PANI-LEB-g-DGEBA copolymer were successfully synthesized from the anionic copolymerization method. Without using this approach, both polymers may only form a polymer blend.

In this work, the PANI-LEB-g-DGEBA copolymer can be found in the form of black solid while PANI-ES-g-DGEBA copolymer was in gel form. We believed the difference of both copolymers was due to the presence of DGEBA homopolymerization. The PANI-LEB-g-DGEBA copolymer which does not have ether linkages was expected to undergo curing alone. As for PANI-ES-g-DGEBA copolymer, the percentage of ether linkages group formed may be succeeding the amount of grafting group thus prevented the curing process of copolymer. This can be figured out from the THF Soxhlet extraction analysis.

It was found that the total monomer conversion of DGEBA in copolymers consisted of grafted sections and DGEBA homopolymers; and also crosslinked section where it might have resulted from the intermolecular Michael reaction on quinoid rings among PANI molecules.²⁰ THF was used in Soxhlet extraction as it will mostly dissolve the oligoether side of

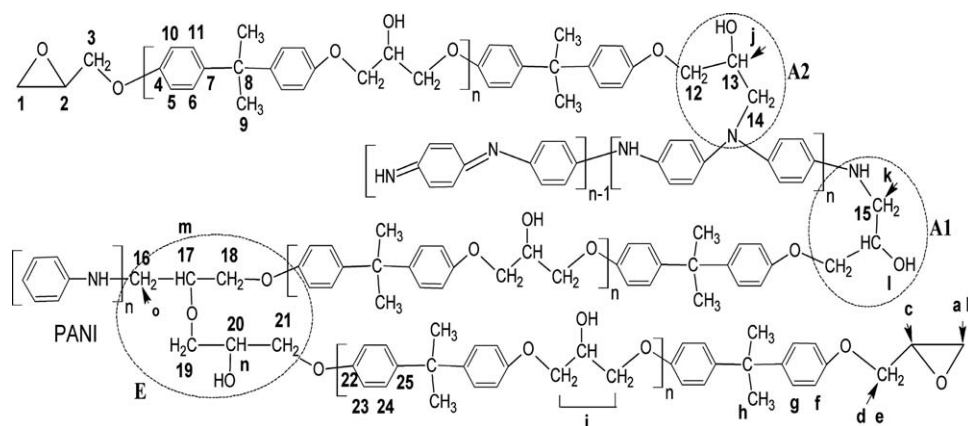


Figure 4 Assignments of ^{13}C and ^1H chemical shifts for PANI-ES-g-DGEBA copolymer where A1, A2, and E represented the grafting on the chain end and center of PANI backbones, and DGEBA homopolymerization, respectively.

copolymer together with grafted section and leaving behind the crosslinked residues. The discussion and interpretation on the crosslinked section of the copolymer after being subjected to Soxhlet extraction via IR analysis was reported elsewhere.²¹

For comparison, the PANI-LEB-g-DGEBA copolymer yielded 51.6% gel content while nearly 8.5% gel content can be obtained from PANI-ES-g-DGEBA copolymer upon Soxhlet extraction. This showed that PANI-ES-g-DGEBA copolymer did not have much crosslinked section formed. The gel content of PANI-LEB-g-DGEBA copolymer was found to have six times higher than PANI-ES-g-DGEBA copolymer. This explained that some of the benzenoid units in PANI-LEB have been oxidized to quinoid units due to instability of PANI-LEB structure at ambient temperature. During the solution preparation of nitrogen anions of PANI-LEB via reaction with NaH in DMSO solution, the nitrogen anions produced are expected to undergo intermolecular Michael reaction on the quinoid moiety thus led to insoluble crosslinked sections before copolymerization with DGEBA conducted.²⁰

Thermal properties

DSC was performed to determine the glass transition, melting point, crosslinked reaction, and decomposition of the copolymers. To have more understanding on the curing behavior of copolymers, the thermal behavior of PANI-ES and PANI-LEB should not be neglected. Figure 5 shows the DSC thermogram of PANI-ES, PANI-LEB, and both copolymers under N_2 atmosphere. It was believed that the PANI-ES powder had discernible moisture content where the first endothermic peak at around 90°C was attributed to the evaporation of moisture. The second endothermic peak at about 260°C was correlated with the loss of HCl dopant.^{32,33} The HCl elimination was due to the presence of oxygen gas in air

which worked as oxidizing agent. The small endothermic peak (at around 320°C) in PANI-ES thermogram was possibly due to the loss of bound water or low molecular weight oligomers.³⁴

For PANI-LEB, it displayed three endothermic peaks at around 96°C , 323°C and more than 450°C which were expected to be due to the evaporation of moisture, loss of bound water or low molecular weight oligomers and decomposition of PANI structure, respectively. Traore et al. found that above 450°C , PANI-LEB will undergo chain scission to produce benzene ring fragmentation products.³⁵

In case of DGEBA-grafted PANI, a sharp exothermic peak can be seen on the thermograms of both copolymers. This means that both copolymers are partially cured. PANI-ES-g-DGEBA copolymer has T_g at about -4.1°C . But for PANI-LEB-g-DGEBA copolymer, the T_g was much higher as it appeared at

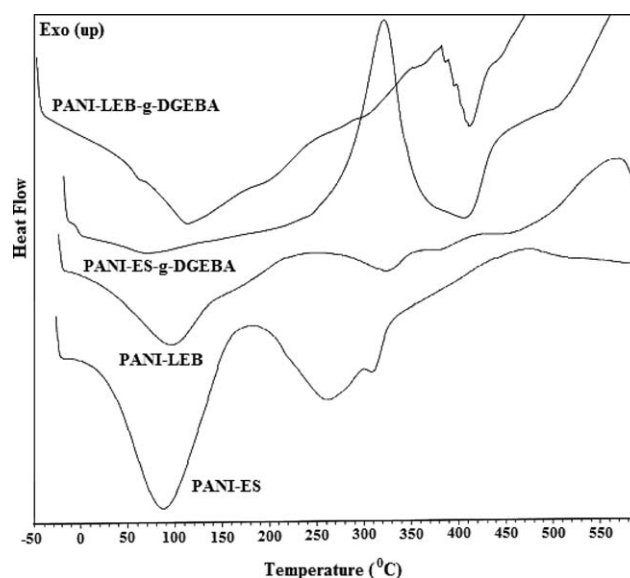


Figure 5 DSC thermograms for PANI-ES, PANI-LEB, PANI-ES-g-DGEBA copolymer, and PANI-LEB-g-DGEBA copolymer.

TABLE I
Curing Characteristics of PANI-LEB-g-DGEBA and PANI-ES-g-DGEBA Copolymers from the DSC Measurement Using Heating Rate of 10°C/min

Copolymers	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
PANI-LEB-g-DGEBA	333	400	412	302.9
PANI-ES-g-DGEBA	289	336	367	283.6

about 60°C. There was also an endothermic peak at 110°C for PANI-LEB-g-DGEBA copolymer where it characterized the evaporation of DMSO residue in the solid copolymer.

On the basis of the curing characteristics of both copolymers given in Table I, the curing started at higher temperature as it was possibly due to the steric hindrance of the benzenoid rings towards the epoxide-amine polyaddition and weak nucleophilicity of secondary aromatic amine groups which behave as electron donors to initiate the curing with DGEBA. A stronger nucleophile can initiate the curing process at lower temperature. Therefore, onset temperature of exotherm (T_i) may be used as criterion for evaluating the relative reactivity of both PANI-ES and PANI-LEB. The PANI-ES-g-DGEBA copolymer has lower T_i than PANI-LEB-g-DGEBA copolymer and this means that the PANI-ES is apparently more reactive.

However, it would be better to use the magnitude of exothermic peak temperature (T_p) for comparison of reactivity of both PANI-ES and PANI-LEB. It was found that PANI-ES-g-DGEBA copolymer has lower T_p than PANI-LEB-g-DGEBA copolymer. Thus, this indicated that PANI-ES was more reactive as nucleophile than PANI-LEB.

Although the PANI-ES and PANI-LEB have almost the same chemical structure, the reactivity of primary aromatic amine-epoxy and secondary aromatic amine-epoxy is different. PANI-LEB is expected to have more secondary aromatic amine groups compared to PANI-ES. The secondary aromatic amine was found to react slower than primary aromatic amine.³⁶ As for DGEBA, there was higher δ^+ charge on the end carbon atom of the epoxy group due to less electronegativity on the central C(CH₃)₂ group. In this work, the molar ratio of DGEBA to both PANI was the same. Thus, it is believed that the presence of O—H groups in PANI-ES-g-DGEBA copolymer resulted from ether linkages formation will explain the reactivity of PANI in copolymer. These O—H groups are expected to act as catalysts for amine-epoxy and hydroxyl-epoxy reactions.²⁹ Thus, it caused the PANI-ES-g-DGEBA copolymer to undergo curing at lower temperature.

Electrical and thermal conductivities

For measurement of electrical and thermal conductivities, PANI-ES-g-DGEBA copolymer was com-

pared with a polymer blend sample of DGEBA - polyeteramine which contained 5 wt % of PANI-ES as filler (5 wt % PANI-ES/DGEBA blend). The electrical and thermal analyses of various samples were summarized in Table II.

The highly electrical resistant DGEBA was found to have much lower electrical conductivity, σ compared with the semi conducting copolymer, PANI-ES. The composites of PANI-ES and DGEBA which were prepared either via chemical synthesis or physical blending had σ value in between the values of both host polymers. The copolymer was found to have σ of 10^0 and 10^3 orders of magnitude higher than that of the polymer blend counterpart and DGEBA, respectively. This means the copolymer was able to conduct electricity as the property of PANI-ES was successfully imparted in the DGEBA. The copolymerization method is expected to produce longer PANI-ES chains for better electron mobility before it was encapsulated by DGEBA matrix. For 5 wt % PANI-ES/DGEBA blend, the particles of PANI-ES are possibly well dispersed in DGEBA matrix and it is expected hard to form a conduction path for electrons mobility. The bulk densities, P was considerably low, which were in the range of 0.8–1.1 g/cm³.

It can be seen that PANI-ES has the highest thermal diffusivity, α among all the samples. The high α value in PANI-ES compared with other three samples is possibly caused by the high order of atoms as reported by Yan et al.³⁷ However, Yan et al. found that there were no correlation between electrical conductivity with the thermal diffusivity and specific heat. It is considered to be originated from the amorphous characteristics of PANI-ES.³⁷ For DGEBA, PANI-ES-g-DGEBA copolymer and 5 wt % PANI-ES/DGEBA blend samples, the α value was almost similar. It is possibly due to the strongly bonded crosslink networks via curing reaction which retarded the molecular vibration upon heating or the heat resistant behavior of DGEBA domain. The heat

TABLE II
Electrical and Thermal Analyses of PANI-ES, DGEBA, PANI-ES-g-DGEBA Copolymer, and 5 wt% PANI-ES/DGEBA Blend

Sample	PANI-ES	DGEBA	PANI-ES-g-DGEBA Copolymer	5 wt% PANI-ES/DGEBA Blend
σ (S/cm)	2.95	3.53×10^{-9}	3.31×10^{-6}	2.82×10^{-7}
p (g/cm ³)	1.12	1.00	1.12	0.83
α (mm ² /s) ^a	0.69	0.13	0.11	0.13
C_p (J/gK) ^a	1.04	1.52	1.69	1.46
k (W/mK) ^a	0.81	0.20	0.21	0.15

^a Measurement of thermal conductivity properties at 303 K

specific values, C_p for all samples were not much varied.

Based on Table II, PANI-ES is found to have thermal conductivity, k value four times higher than the DGEBA. However, the addition of 5 wt % PANI-ES in the preparation of copolymer or polymer blend did not show promising results. PANI-ES-g-DGEBA copolymer has 0.01 W/mK higher than DGEBA and may be considered as no improvement at all while 5 wt % PANI-ES/DGEBA blends has 0.05 W/mK lower than DGEBA. This shows that insertion of PANI-ES in DGEBA did not really help on thermal conductivity property. As explained by Jagannathan et al., strong phonon scattering in amorphous materials such as PANI-ES usually results in low thermal conductivity.³⁸ However, it was found that the copolymer has better thermal conductivity than its polymer counterpart.

CONCLUSIONS

The anionic copolymerization which was employed in this work successfully produced the PANI-g-DGEBA type copolymers. The grafted sections in copolymers were able to be identified as it occurred on the center and chain end of PANI backbones in copolymers. The copolymer molecular characterization was confirmed by the FTIR, ¹³C and ¹H NMR analysis. However, PANI-ES-g-DGEBA copolymer has additional side reaction due to DGEBA homopolymerization as it was not found in the PANI-LEB-g-DGEBA copolymer. The competition between DGEBA homopolymerization and grafting in PANI-ES-g-DGEBA copolymer caused not much crosslink sections formed in the copolymer as determined by Soxhlet extraction. It was found that PANI-LEB which has more benzenoid units compared to PANI-ES tends to create more crosslinked sections in resultant copolymer as PANI-LEB is easily oxidized to typical PANI-EB. As analyzed from DSC thermogram, the PANIs were also involved in curing reaction with DGEBA and it was believed that the grafting was part of curing process in copolymers. The oxidation states of PANI were found to affect the grafting mechanism and the properties of copolymer.

Although the electrical conductivity of copolymer was enhanced with the presence of PANI-ES but the thermal conductivity was not improved at all. Therefore, it was believed that there was no correlation between electrical conductivity with thermal conductivity as PANI-ES behaves as amorphous material. However, it was found that chemically modified PANI-ES with DGEBA has slightly better electrical and thermal conductivity than its polymer blends counterpart.

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